Influence of Nanoscale $Fe_{(1-x)}S$ Particles on Coal Liquefaction

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ABSTRACT

It has been shown that during the process of coal liquefaction, iron based catalyst precursors transform to pyrrhotite in the presence of sufficient sulfur. Due to this transformation, the activity of the catalyst initially added relative to the transformed catalyst is not known. In an attempt to address this question, the activity of nanoscale particles of pyrrhotite ($Fe_{1-x}S$), generated by a laser pyrolysis technique, is being studied for the direct liquefaction of a subbituminous coal. Their activity is being compared to that of a similarly prepared iron carbide that is sulfided in situ. The particles produced by this technique have a similar size range and distribution. Comparative studies of the changes in phase and particle size of the catalysts during coal liquefaction experiments are determined by XRD and Mössbauer spectroscopy.

INTRODUCTION

The utility of iron based coal liquefaction catalysts has been known for almost a century. The basis for their use is a combination of moderate activity and relatively low cost, compared to more active catalysts such as Mo, Ti, Ni, etc. A "red mud" iron oxide catalyst precursor was first used in commercial coal liquefaction. It was found that the addition of sulfur with the iron oxide precursor improved the processing of low sulfur coals.[1] Since then, numerous studies have examined different iron phases such as oxides, sulfides, carbides, and organometallic compounds as catalyst precursors. In most of these studies the addition of a source of sulfur has been shown to increase the catalyst activity and selectivity.

Three methods are generally used to introduce the catalyst to the coal. The first is the

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physical mixing of a finely divided solid catalyst into the coal feed slurry. This is relatively straightforward and has been used extensively. The second is the addition of an oil-soluble catalyst precursor, such as iron pentacarbonyl, to the coal feed slurry. This method allows almost infinite initial dispersion of the iron. The third method is the addition of the iron to the coal itself, using either an ion exchange technique or by precipitation of a water soluble iron compound within the coal matrix. The former method can only be applied to low rank coals.

Regardless of the method of addition or the precursor composition, in the presence of sulfur the final form of the iron is generally pyrrhotite. Many studies propose that pyrrhotite $(Fe_{1-x}S)$[2,3,4,10] is the active form of iron based catalysts. Indeed, pyrrhotite is the thermodynamically favored phase under liquefaction conditions in the presence of sufficient sulfur. Research has shown that a variety of iron based precursors including oxides[10], sulfides[5,6], carbides[13], and carbonyls[2,3,9] are transformed to pyrrhotite during coal liquefaction.

Some studies have been made of the kinetics of transformation of the precursor to the sulfide. Montano et al. [5,6] used in situ Mössbauer spectroscopy to study the decomposition of pyrite, to pyrrhotite and H_2S, in hydrogen and under liquefaction conditions. It was found that the onset of the transformation to pyrrhotite occurs at ~300°C and is nearly complete at ~400°C. The activation energy of the transformation decreased with decreasing particle size. Larger pyrite particles were reported to break during the transformation yielding smaller pyrrhotite particles. It was concluded that both H_2S and pyrrhotite are active as catalysts for the liquefaction process. Others have attributed the catalytic activity of pyrite to H_2S alone[11], arguing that the low surface area of pyrite should make it a very poor catalyst. This view agrees with the finding that pyrite and pyrrhotite do not exhibit any catalytic effect for the gasification of graphite[14]. The view of a synergistic effect between pyrrhotite and H_2S has been reached by other workers using both pyrite and iron oxide[10].

In a study of the liquefaction of a Victorian brown coal [8l], using hematite, iron carbonyl, and impregnated iron acetate as catalyst precursors, it was concluded that, in the absence of added sulfur, the active form of the iron catalyst was reduced α-Fe. This concurs with the results of a study which found that metallic iron promoted the catalytic hydrogenation of graphite at temperatures below 1000 °C while pyrite and pyrrhotite showed no catalytic activity[14]. More recently, Weng et al.[15] have proposed that, while a synergistic effect between pyrrhotite and H_2S promotes coal liquefaction, γ-Fe is a more active catalyst than pyrrhotite. The fact that a substantial amount of Fe_3C was also formed during the reaction may indicate that insufficient sulfur was present for conversion of the precursor to pyrrhotite. This may be the reason for the γ-Fe formation.

As this brief summary indicates, the relationship between the phase of the iron catalyst and its activity is not fully understood. Neither is there any clear information

about the kinetics of precursor sulfiding, and the factors which influence this reaction. The relevance of these statements is that, even assuming that iron sulfide is an active liquefaction catalyst, the active phase may not be present during some of the critical initial reactions of coal dissolution.

The purposes of this work are to attempt to resolve\ these questions through: examining the effect of nanoscale iron carbide catalyst on coal liquefaction: determining the kinetics of *in-situ* sulfiding of the iron carbide; and comparing the performance when the catalyst is added in the form of nanoscale pyrrhotite. Both phases of the iron will be formed by a laser pyrolysis technique, described in detail elsewhere[13], which will ensure that the precursor particles have approximately the same size distribution. Previous studies have shown that the Fe_7C_3 particles transform to pyrrhotite, in the presence of added sulfur under liquefaction conditions, while retaining their small size[13]. By comparing the activity of the presulfided catalyst to the catalyst sulfided *in situ* , the relative activity of the two may be defined. This will allow a better appreciation of the importance of sulfiding kinetics, and the attainment of the active phase, to be determined.

EXPERIMENTAL

The coal used is a -200 mesh subbituminous Black Thunder coal which is stored in sealed foil bags prior to use, in order to reduce the effects of air oxidation. The native iron content of the coal is 0.17wt%. In liquefaction experiments 3 grams of coal and 5 grams of tetralin are charged into a 50 ml stainless steel tubing bomb reactor. The catalyst loading is 1 wt% Fe to coal. The reactors are constructed with a horizontal orientation to reduce any mass transfer limiting effects. Dimethyl disulfide (DMDS) is added at 120% of the calculated amount required for transformation of the precursor to pyrite. The sealed bombs are purged and pressurized with hydrogen to 1000 psig (cold) prior to reaction.

The bombs are agitated vertically at ~400 cycles/min while immersed in a heated fluidized sand bath. The reactions are carried out for up to 30 minutes, and at temperatures between 385°C and 415°C. Following reaction, the tubing bomb is removed from the heated sand bath and quenched in a cool sand bath. A gas sample is taken from the cooled reactor and analyzed by GC.

The products of the liquefaction experiments are analyzed by solubility class. The reactor contents are extracted with THF to determine the total conversion to THF soluble products. The THF solubles are then precipitated with pentane. The pentane soluble product is defined as the oil fraction while the insoluble portion is defined as the preasphaltene + asphaltene fraction. The THF insoluble fraction is defined as the IOM fraction. The gas yield is determined by GC and the oil yield is determined by difference.

The spent catalyst is contained in the IOM fraction and is characterized by XRD and Mössbauer spectroscopy to determine the phase and approximate size of the iron based catalyst after reaction.

RESULTS

In order to determine the behavior of the iron carbide particles under liquefaction conditions, tubing bomb experiments were carried out in the absence of added coal. As reported elsewhere[13], it was determined by XRD that the iron carbide particles transform to pyrrhotite in the presence of added sulfur within 30 min at 385°C. Further, analysis of TEM micrographs show that the particles retain their small size and relatively narrow size distribution, with the exception of the formation a few larger crystallites.

In liquefaction studies using a subbituminous Wyodak coal the iron carbide showed moderate catalytic activity, similar to that of iron pentacarbonyl. The catalyst loading in both cases was 1 wt% Fe. The iron carbide increased the total conversion by ~10% over the thermal baseline in the temperature range from 350°C to 440°C. Further, the catalyst caused an apparent increase in the selectivity to oils over the temperature range ~350°-400°C.

The method of production of the nanoscale iron carbide particles by laser pyrolysis has been reported elsewhere.[13] A modification of this process was used to produce the nanoscale pyrrhotite. A reactant gas stream of ethylene and hydrogen sulfide is intersected with the beam from a tunable CO_2 laser. The pyrrhotite particles are formed in the small pyrolysis zone formed at this intersection. The size of the particles can be controlled by adjusting the reaction parameters. XRD has identified the phase of the particles as $Fe_{(1-x)}S$ with an average diameter of ~10nm.
Work is currently in progress to determine the catalytic activity of the nanoscale pyrrhotite particles as well as their behavior during the liquefaction process.

SUMMARY

The results of this study will allow the kinetics of the transition of iron carbide to the sulfide to be determined, and whether the transformation is sufficiently rapid so that an active catalyst is present during coal dissolution. By using two different catalysts produced by the same technique the influence of size effects on the activity are reduced. XRD and Mössbauer spectroscopy are used to determine the phase of the catalyst after the reaction. The relative importance of attainment of the active phase during the initial stages of liquefaction will be discussed.

ACKNOWLEDGEMENTS

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